Chemical Synthesis *via* Metal Atoms: Preparation and *X*-Ray Structure of (1,3-η^3-Cyclo-octa-5,6-dienyl)bis(triphenylphosphine)rhodium(I)

Giovanni Vitulli,*[a] **Andrea Raffaelli,**[a] **Paolo A. Costantino,**[a] **Carlo Barberini,**[a] **Fabio Marchetti,**[b] **Stefano Merlino,**[b] **and Philip S. Skell**[c]

[a] *Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica, and* [b] *Istituto di Chimica Generale, Istituto di Mineralogia e Petrografia, Facoltà di Scienze M.F.N., Università di Pisa, Pisa, Italy*

[c] *Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.*

Co-condensation of Rh vapour with cyclo-octa-1,5-diene followed by addition of a toluene solution of PPh_3 yields the title compound which has been characterized by *X*-ray crystallography.

Rhodium vapour, conveniently prepared by resistive heating of a tungsten wire surface coated with electrodeposited rhodium, was co-condensed at -196 °C with cyclo-octa-1,5-diene, in a glass reactor built as reported elsewhere,[1] using an electrical input of 50 A at 12 V. Addition of a toluene solution of PPh_3 to the yellow-brown matrix resulted, on melting and mixing, in the formation of a solution stable at room temperature from which yellow-orange crystals of the title compound, $(C_8H_{11})Rh(PPh_3)_2$ (**1**) m.p. 152—155 °C (decomp.), were obtained following evaporation and addition of n-pentane. From runs in which 100—150 mg of metal were vaporized, the pure product was isolated in yields of 30—40%. Satisfactory elemental analyses have been obtained. An interesting feature of these rhodium vapour experiments is the apparent absence of bulk rhodium among the reaction products. The *X*-ray structural determination of (**1**) was undertaken.

Crystal data: $RhC_{44}H_{41}P_2$, $M = 734.7$, triclinic, space group $P\bar{1}$, $a = 14.519(4)$, $b = 11.504(3)$, $c = 11.126(3)$ Å, $\alpha = 101.84(2)$, $\beta = 100.57(2)$, $\gamma = 86.354(1)°$, $U = 1787$ Å^3, $Z = 2$, $D_c = 1.365$ g cm^{-3}. The intensities of 2680 reflections were measured on a Philips PW1100 diffractometer using graphite monochromated Mo-K_α radiation, ignoring the reflections whose intensities were weaker than a threshold value, to θ_{max} of 23.4°. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least-squares calculations using anisotropic thermal parameters for all heavy atoms. The hydrogen atoms of triphenylphosphine were introduced in calculated positions while those of the cyclo-octadienyl ligand were found from a difference-Fourier map. The final residual R is 0.042.†

The structure of the complex (**1**) is shown in Figure 1 together with some important bond parameters. The structure consists of a co-ordinatively unsaturated mononuclear rhodium(I) atom co-ordinated to two phosphorus atoms and to a tri-*hapto*-bonded cyclo-octadienyl ligand. The co-ordination geometry at Rh is almost square planar, the Rh,

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

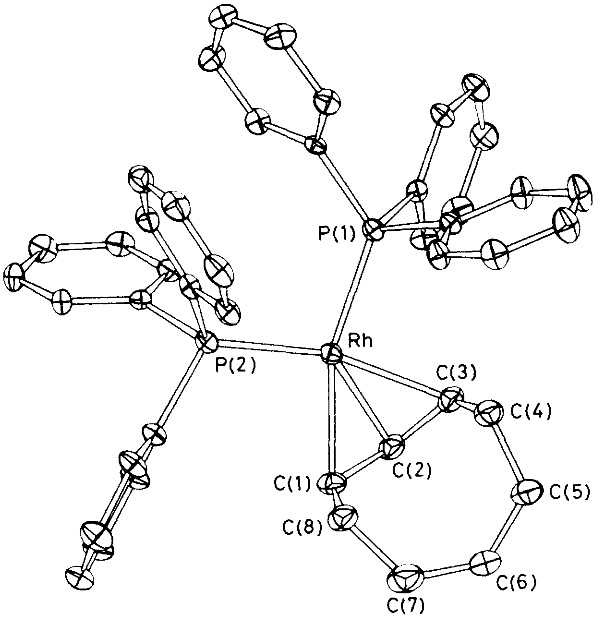

Figure 1. Molecular structure of $(C_8H_{11})Rh(PPh_3)_2$ (**1**). Bond lengths: Rh–P (1), 2.253(3); Rh–P(2), 2.252(3); Rh–C(1), 2.21(1); Rh–C(2), 2.12(1); Rh–C(3), 2.23(1); C(1)–C(2), 1.40(2); C(2)–C(3), 1.39(2); C(3)–C(4), 1.49(2); C(4)–C(5), 1.48(2); C(5)–C(6), 1.42(3); C(6)–C(7), 1.49(3); C(7)–C(8), 1.48(2); C(8)–C(1), 1.51(2) Å. Bond angles: P(1)–Rh–P(2), 102.5(1); P(1)–Rh–C(3), 92.5(4); P(2)–Rh–C(1), 97.2(4); C(1)–Rh–C(3), 67.4(5); C(1)–Rh–C(2), 37.6(5); C(2)–Rh–C(3), 37.1(6)°.

P(1), P(2) atoms and the respective centres of the C(1)–C(2) and C(2)–C(3) bonds of the allyl system being coplanar to within 0.03 Å.

The C(1), C(2), and C(3) atoms of the allyl group are in a plane at 71° with respect to the co-ordination plane and have Rh–C distances (mean value 2.11 Å) close to those found in similar compounds,[2] while the C(5)–C(6) bond length (1.42 Å) is somewhat longer than the length generally reported for unco-ordinated double bonds in cyclo-olefinic moieties.[3] This may be related to the high value of the torsional angle C(4)–C(5)–C(6)–C(7) (*ca.* 50°) which imparts a severe torsional strain to the eight-membered ring.

The complex is sparingly soluble in common organic solvents; it is very air-sensitive in solution, but mildly sensitive in the solid state. The i.r. spectrum of (**1**) (KBr disc) shows a weak band at *ca.* 1630 cm^{-1} which can be tentatively assigned to the C=C stretching mode of the unco-ordinated double bond. A broad ^1H n.m.r. spectrum was obtained at room temperature using $[^2H_8]$toluene as solvent; the complex, however, slowly decomposes in solution, preventing extensive n.m.r. studies.

Isolation of pure characterizable compounds from the reaction of Rh vapour and cyclo-octa-1,5-diene, in the absence of additional stabilizing ligands, has proved difficult. The product obtained in this case is a yellow-brown air-sensitive oil, soluble in aliphatic and aromatic solvents which exhibits a very complex ^1H n.m.r. spectrum, suggesting a mixture of compounds involving extensive rearrangements.

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References

1 See for example, K. J. Klabunde, P. L. Timms, P. S. Skell, and S. D. Ittel, *Inorg. Synth.*, 1979, **19**, 59.
2 J. Pichardt and H. O. Sthüler, *Chem. Ber.*, 1980, **113**, 1623.
3 J. Muller, H. O. Sthüler, G. Huttner, and K. Scherzer, *Chem. Ber.*, 1976, **109**, 1211.